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(54) Branched polyamidoamines, method for their preparation and method of improving the wet strength of paper using them.

(57) Branched polyamidoamines bearing a plurality of pendant aminoamide moieties exhibit properties which are superior to linear polyamidoamines from which the branched polymers are derived. The branched polyamidoamine is readily prepared by reacting a linear polyamidoamine with an alkyl acrylate or methacrylate to prepare a polymer with pendant ester moieties. The ester moieties are then reacted with an alkylene diamine or a polyalkylene polyamine to produce the pendant aminoamide groups. Ammonium polyamidoamines are prepared by contacting the branched polyamidoamine with an epihalohydrin to form curable ammonium moieties on the branched polyamidoamines. The branched polyamidoamines are particularly useful as curing agents for epoxides; as a demulsification agent, flocculant or dye retention agent. Ammonium polyamidoamines are particularly useful as agents for imparting superior wet strength properties to paper.

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- 1 -

BRANCHED POLYAMIDOAMINES, METHOD FOR  
THEIR PREPARATION AND METHOD OF IMPROVING  
THE WET STRENGTH TO PAPER USING THEM.

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The invention relates to branched polyamidoamines and a process for preparing same. In particular, novel polymers bearing a plurality of pendant amidoamine moieties are disclosed.

5           This invention also relates to ammonium polyamidoamines and to their use in the manufacture of paper.

As disclosed in U.S.P. 3,445,441, polyamidoamines are useful as demulsifiers, corrosion inhibitors,  
10 and flocculants for the clarification of water. These polyamidoamines are normally produced by reacting nearly stoichiometric amounts of an alkyl acrylate with a polyamine such as polyalkylene polyamine. Unfortunately, such polymers, which are not curable, often do  
15 not have sufficient molecular weight to be useful in many applications requiring viscosity enhancement and/or high flocculant capability.

U.S.P. 3,305,493 discloses the use of thermosetting adducts of the polyamidoamines and epichlorohydrin in the sizing of paper. Although such thermosetting  
20 adducts, after increase in molecular weight through

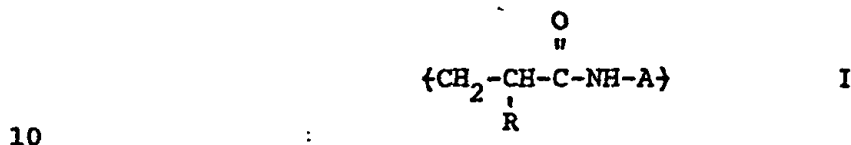
cross-linking, have sufficient molecular weight to be useful in many applications, it is difficult to control the cross-linking reaction so that the formation of unwanted gels is prevented. On the other hand, if the  
5 cross-linking reaction is stopped prematurely, the resulting product does not exhibit the desired activity.

U.S. Patent 3,200,106 discloses a variety of derivatives of high molecular weight polyalkylene polyamines. One of these products is the condensation  
10 product of the polyamine with an alkyl acrylate. This condensation product bears pendant ester groups.

The novel branched polyamidoamines described herein possess several unique and surprising properties not shared by the substantially linear polyamidoamines  
15 described in the prior art. The branched polyamidoamines which bear a plurality of terminal primary amines possess exceptional utility as curing agents for epoxides. Those branched polyamidoamines bearing a plurality of terminal tertiary amine groups exhibit unexpected  
20 activity relative to linear polyamidoamines in the demulsification of oil in water emulsions. The branched polyamidoamines also exhibit enhanced performance as flocculants and dye retention additives.

In view of the foregoing deficiencies of the  
25 conventional polyamidoamines, it is also highly desirable to provide a polymer that has reproducible characteristics and has sufficient activity to be useful in applications such as wet strength additives in the manufacture of paper and the like.

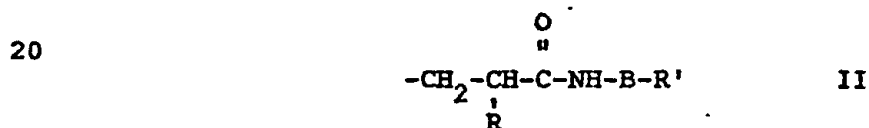
More particularly, the invention resides in a branched polyamidoamine having a weight average molecular weight of at least about 550, as determined by low-angle laser light scattering. This polyamidoamine consists essentially of units corresponding to the formula I



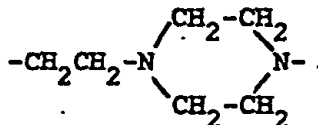
wherein R at each occurrence is independently hydrogen or lower alkyl, e.g., methyl or ethyl; A is



wherein m is an integer from 2 to 6 and n is an integer from 1 to 3; D at each occurrence is independently -H or corresponds to the formula II



wherein R is as defined hereinbefore, B is



-4-

wherein x is an integer from 2 to 10, y is an integer from 1 to 6, and R' at each occurrence is independently -H, a C<sub>1</sub> to C<sub>4</sub> alkyl, or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl. At least about 10 percent, preferably at least about 30 percent, of the groups represented by D correspond to formula II.

The present invention also resides in ammonium polyamidoamines bearing pendant ammonium moieties having cross-linking functionality. Surprisingly, while such ammonium polyamidoamines are very effective as wet strength additives in the manufacture of paper, the paper which has been treated with such ammonium polyamidoamines is sufficiently brokable that it can be recycled.

Another aspect of this invention resides in a method for preparing ammonium polyamidoamines by contacting the branched polyamidoamine with an epihalohydrin under conditions sufficient to form pendant curable ammonium moieties on the branched polyamidoamine.

In yet another aspect, this invention is a method for improving the wet strength of paper by contacting the paper pulp with an amount of the ammonium polyamidoamine which is effective to increase the wet strength of the paper sheet formed from said pulp when said sheet is subjected to conditions sufficient to cross-link the polyamidoamine.

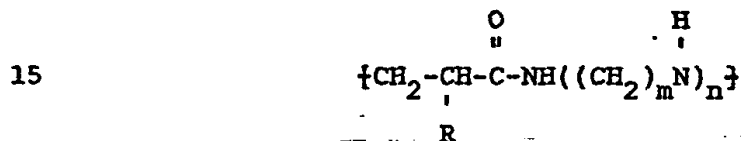
In addition to their utility in the manufacture of paper, the ammonium polyamidoamines of this invention are also useful as flocculants, dimension

-5-

stabilizers for textiles such as wool, tie coat adhesives and the like.

Linear polyamidoamines are conveniently prepared in the manner described in U.S.P. 3,305,493.

5 In general, the essentially linear polyamidoamine is prepared by contacting an alkylenediamine or a polyalkylene polyamine with the ethylenically unsaturated carboxylic compound, e.g., alkyl acrylate or methacrylate, acrylamide, acrylic acid or methacrylic acid, under  
10 reactive conditions. Preferably, the foregoing reactants are employed in stoichiometric ratio to form a linear polyamidoamine represented by the formula:



wherein R, m and n are as defined hereinbefore.

Advantageously, the linear polyamidoamine has a weight  
20 average molecular weight (Mw) of at least about 500, preferably at least 1000, most preferably from 3000 to 10,000.

When converting the linear polyamidoamine to a branched polyamidoamine, the linear polyamidoamine is  
25 contacted with an ethylenically unsaturated carboxylic compound under conditions sufficient to produce a Michaels addition reaction between an amine moiety of the linear polyamidoamine and the ethylenically unsaturated moiety of the carboxylic compound. Exemplary  
30 carboxylic compounds include  $\alpha, \beta$ -ethylenically unsaturated carboxylic acids such as acrylic acid and methacrylic acid;  $\alpha, \beta$ -ethylenically unsaturated amides such

-6-

as acrylamide and methacrylamide; and esters of  $\alpha, \beta$ -ethylenically unsaturated acids derived from primary alcohols having from 1 to 10 carbons. Of the foregoing carboxylic compounds, methyl acrylate and acrylamide  
5 are preferred, with methyl acrylate being especially preferred. The reaction of the unsaturated carboxylic compound with the linear polyamidoamine should be performed at a temperature at which substantial cross-linking of the polymer is avoided. Generally, such  
10 temperature is in the range from 0° to 200°C, with temperatures of from 20° to 100°C being preferred. While the foregoing reaction can be conducted neat, it is generally desirable to employ a diluent which is a solvent for the polyamidoamine but which is substantially  
15 inert to the reactants. Water and lower alkanol, having from 1 to 4 carbons, are generally preferred diluents with methanol being most preferred.

The ratio of equivalents of the aforementioned unsaturated carboxylic compound to the equivalents of  
20 amino hydrogens present in the linear polyamidoamine can be varied to produce the desired substitution of pendant carboxylic groups on the polyamidoamine. If complete substitution is desired, a stoichiometric amount or an excess of the unsaturated carboxylic  
25 compound can be employed. However, if a lesser degree of substitution is desired, the reactants can be combined in the desired ratio and essentially completely reacted. The progress of this reaction can be monitored by infrared spectrophotometric analysis or other tech-  
30 niques known in the art. It is advantageous that at least 50 mole percent of the total amino hydrogens of the linear polyamidoamine be reacted with the unsaturated carboxylic compound in order to provide the

-7-

ultimate ammonium polyamidoamine with the unique properties and advantages characteristic of the polymers of this invention. Preferably, at least about 75 mole percent of amino hydrogens are reacted with polymers  
 5 having from 90 to 100, mole percent of amino hydrogens reacted being most preferred.

In this form, the polyamidoamine bears pendant groups corresponding to the formula:



wherein R is as defined hereinbefore and Q is OH, NH<sub>2</sub>  
 15 or alkoxy having from 1 to 10 carbon atoms. It is understood that the moieties represented by Q may be the same or different in the same molecule of the polyamidoamine. For example, if a single unsaturated carboxylic compound is reacted with the linear poly-  
 20 amidoamine, all of the moieties represented by Q will be the same. However, if a mixture of unsaturated carboxylic compounds, e.g., acrylic acid and acrylamide is employed, then the moieties represented by Q will be different. In order to form the desired branched  
 25 polyamidoamine, this polyamidoamine bearing pendant carboxylic groups is reacted with an alkylenediamine or polyalkylene polyamine, which optionally bears hydroxyl alkyl moieties. However, prior to the introduction of the alkylenediamine or polyalkylene polyamine, it is  
 30 desirable to remove essentially all unreacted carboxylic compounds, usually by distillation. The amount of alkylenediamine or polyalkylene polyamine employed is



that amount which is sufficient to suppress cross-linking of the polyamidoamine which can occur through the pendant carboxylic moieties. Beneficially, the alkylenediamine or polyalkylene polyamine is employed in a 200 to 300 mole percent excess, the pendant carboxylic moieties on the polyamidoamine. Exemplary alkylenediamines which can be reacted with the polyamidoamine having pendant carboxylic groups include ethylenediamine, propylenediamine and hexamethylenediamine. Illustrative polyalkylene polyamines include diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. Also suitable are aminoethanolamine and N,N-dimethylethylenediamine. Of the foregoing amines, ethylenediamine and diethylenetriamine are preferred, with ethylenediamine being especially preferred.

The conditions which are desirable to promote the reaction of the polyamidoamine bearing the pendant carboxylic moieties with the alkylenediamine or polyalkylene polyamine will vary depending upon the carboxyl moiety (Q) of the pendant moiety. If Q is alkoxy, the reaction is a simple amidation of the pendant ester groups on the polyamidoamine which proceeds under relatively mild conditions, e.g., temperatures in the range from 20° to 200°C. This amidation of ester can be performed neat, but is preferably carried out in an inert diluent in which the polyamidoamine and the alkylenediamine or polyalkylene polyamine are soluble. While water is generally the preferred diluent in such an amidation reaction, it is generally desirable to minimize hydrolysis of the ester groups which can occur at higher temperatures by employing an excess of the diamine or polyamine reactant. Methanol and other

-9-

lower alkanols are also advantageously employed as diluents in this mild amidation reaction.

In instances wherein Q is hydroxyl (OH) or amino ( $\text{NH}_2$ ), it is necessary to employ more severe reaction conditions, e.g., temperatures in the range from 125° to 200°C, with temperatures from 150° to 190°C being preferred. Generally, in these reactions, a diluent is not necessary.

The time required to effect substantially complete reaction by either of the foregoing procedures will vary depending upon the reaction temperature and other factors such as the degree of substitution desired. Following completion of the reaction, the branched polyamidoamine is conveniently recovered by a distillation of solvents and/or byproducts from the polymer at reduced pressure.

The following examples are given to illustrate embodiments of the invention and should not be construed as limiting its scope. In these examples, all parts and percentages are by weight unless otherwise indicated.

#### Example 1

##### A. Preparation of Linear Polyamidoamine

Into a 250-ml three-neck round bottom flask equipped with a reflux condenser, air driven stirrer and addition funnel is charged 60.1 g (1 mole) of ethylenediamine. To the flask is then added with stirring 86.09 g (1 mole) of methyl acrylate by dripping it slowly into the flask over a period of 35 minutes. The temperature of the reaction mixture rises

-10-

to 70°C during this addition and analysis of the reaction mixture using proton nuclear magnetic resonance indicates that all of the double bond has disappeared. The reflux condenser and addition funnel are replaced  
5 with a nitrogen sparge and a distillation apparatus. Using a steam bath, the reaction mixture is heated to 90°-95°C for 24 hours. After this time, the reaction mixture is a very viscous, light yellow amorphous solid. Analysis of this reaction mixture indicates  
10 that all of the ester moieties have reacted thereby yielding a linear polyamidoamine having a weight average molecular weight (Mw) as determined by light scattering of 4000-8000.

#### B. Preparation of Branched Polyamidoamine

15 The aforementioned linear polyamidoamine is diluted with water to 65 percent solids. A 50 g portion of this solution is charged into a 250 ml three-neck round bottom flask equipped with stirrer and reflux condenser and 24.54 g (stoichiometric amount with  
20 respect to amino hydrogens of the linear polyamidoamine) of methyl acrylate is added at one time. The temperature of the reaction mixture increases from ambient to 35°C and is then heated with stirring at 80°C for four hours. Analysis of the reaction mixture  
25 at this point indicates approximately 95 percent of the methyl acrylate has been added to the polymer to provide a linear polyamidoamine having carboxylate ester branches. To this material is added approximately 70 g of ethylenediamine (4 moles of ethylenediamine per mole  
30 of ester) and the heating of the reaction mixture is continued for an additional four hours. Analysis of this mixture using proton NMR indicates complete conversion of the ester moieties to amide moieties.

Excess ethylenediamine, methanol and water are removed using a water aspirator vacuum at 60°-95°C.

#### Example 2

To a 250 ml flask was charged 109.2 grams of  
5 the linear polyamidoamine prepared in the first reaction  
in Example 1 and 50 ml of  $\text{CH}_3\text{OH}$ . The flask was equipped  
with a stirrer, a condenser and a means for measuring  
temperature. To the polyamidoamine was added 27.49  
10 grams of methyl acrylate dropwise with stirring at an  
initial temperature of 20°C. This addition introduces  
1 equivalent of methyl acrylate for every 3 equivalents  
of amino hydrogens in the polyamidoamine. The temperature  
of the reaction mixture rose to 40°C during addition of  
the methyl acrylate. Immediately following the addition  
15 of the acrylate, 61.5 grams of ethylene diamine was  
introduced. The reaction mixture was then heated at  
80°C for 18 hours at 90°C. The methanol and excess  
ethylene diamine were removed by distillation at reduced  
pressure. The resulting polymer was light tan in color  
20 and a tacky solid which was soluble in water or methanol.

#### Example 3

To a 500 ml flask was charged 165.9 grams of  
the linear polyamidoamine prepared in the first reaction  
in Example 1 and 100 grams of  $\text{CH}_3\text{OH}$ . The flask was  
25 equipped with a stirrer, a condenser and a means for  
measuring temperature. To the polyamidoamine was added  
dropwise 41.5 grams of methyl acrylate at a temperature  
of 70°C. Immediately following the addition of the  
acrylate, 43.4 grams of N,N-dimethyl ethylen diamine  
30 was added to the reaction mixture. The reaction mixture

-12-

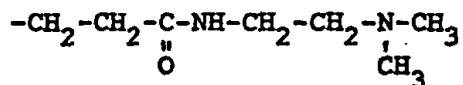
was heated at 115°C for 72 hours. The reaction mixture was then distilled to remove methanol. The resulting tacky, orange polymer was analyzed by proton magnetic resonance and infrared spectrophotometry and was  
 5 determined to be a branched polyamidoamine bearing a plurality of pendant tertiary amine groups.

Examples 4 and 5 indicate that a branched polyamidoamine is a more powerful demulsifier than its linear counterpart.

10 Example 4

A biphasic liquid containing 95 percent tap water and 5 percent crude oil was combined with 50 parts per million (ppm) of a sodium salt of petroleum sulfonate. This liquid was blended at high speed for 5  
 15 minutes to prepare a stable emulsion. A linear polyamidoamine prepared from ethylene diamine and methyl acrylate and having a molecular weight of 1500 was charged to samples of the emulsion at loadings of 25, 50, 100 and 250 ppm. After 12 hours, no demulsification  
 20 was observed.

A branched polyamidoamine having a molecular weight of about 2000 was tested as a demulsifier. This polymer was prepared by converting 30 percent of the amino hydrogens on the above-described linear polyamido-  
 25 amine to groups of the formula



-13-

by sequential reaction of the linear polyamidoamine with methyl acrylate and then N,N-dimethyl ethylene diamine.

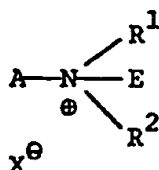
5 The branched polyamidoamine was introduced to samples of the aforementioned oil emulsion at loadings of 25, 50, 100 and 250 ppm. At the 100 ppm loading the emulsion yielded a clear aqueous phase after 12 hours. The branched polyamidoamine exhibited no demulsification activity at the other loadings tested.

10 Example 5

In a manner otherwise similar to Example 4, an oil-in-water emulsion was prepared using 250 ppm sodium oleate in place of the sodium salt of the petroleum sulfonate. The linear polyamidoamine described in  
15 Example 4 was charged to samples of the emulsion at loadings of 25, 50 and 74 ppm. Demulsification was observed after 1 hour only at the 74 ppm loading.

The branched polyamidoamine described in Example 4 was charged to samples of the emulsion at  
20 loadings of 25, 50 and 74 ppm. Demulsification was observed after 1 hour at the 25 ppm loading.

Ammonium polyamidoamines of this invention are advantageously characterized as having a polyamido-amine backbone bearing at least one pendant cross-linking  
25 ammonium moiety. Such ammonium moiety, hereinafter also referred to as  $Z^{\oplus}$ , is represented by the formula:



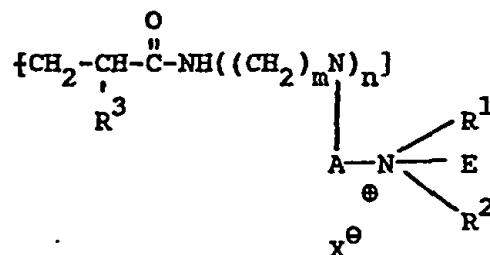
5  
 10 wherein each  $\text{R}^1$  and each  $\text{R}^2$  are independently hydrogen, halohydroxyhydrocarbyl, hydrocarbyl, hydroxyhydrocarbyl or aminohydrocarbyl, wherein amino is a secondary or tertiary amino; E is a monovalent hydrocarbon radical bearing an epoxy group or a group or groups capable of being converted to an epoxy group or E and  $\text{R}^1$  are collectively a propylene radical or substituted propylene radical



15  
 20 wherein the  $\alpha$ -carbon substituents, if any, are  $\text{C}_1$ - $\text{C}_3$  alkyl and the  $\beta$ -carbon substituent, if any, is hydroxy, halo, hydrocarbyl or hydroxyhydrocarbyl; A is a divalent organic radical, e.g., alkylene or amidoamino; X is a monovalent or polyvalent anion common to conventional ammonium salts. For the purposes of this invention, the term "hydrocarbyl" is defined as a monovalent  
 25 hydrocarbon radical such as alkyl, cycloalkyl, aryl, alkenyl and the like. Preferred ammonium polyamidoamines have at least one quaternary ammonium repeating unit represented by the formula:

-15-

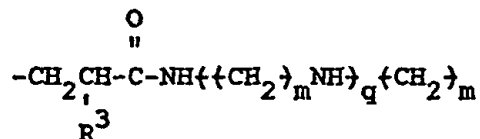
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- 10 wherein A, E, X, R<sup>1</sup> and R<sup>2</sup> are as defined before except  
 that neither R<sup>1</sup> nor R<sup>2</sup> is hydrogen; each R<sup>3</sup> is indepen-  
 15 dently hydrogen or lower alkyl, e.g., methyl or ethyl,  
 each m is a whole number from 2 to 6; and n is a whole  
 number from 1 to 3, more preferably 1 or 2, most  
 preferably 1.

In the more preferred quaternized polyamido-  
 amines, A is an amidoamino radical represented by the  
 formula:

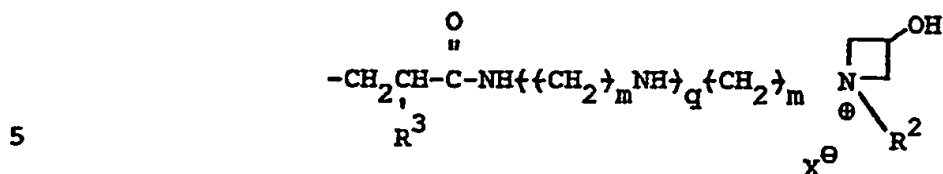
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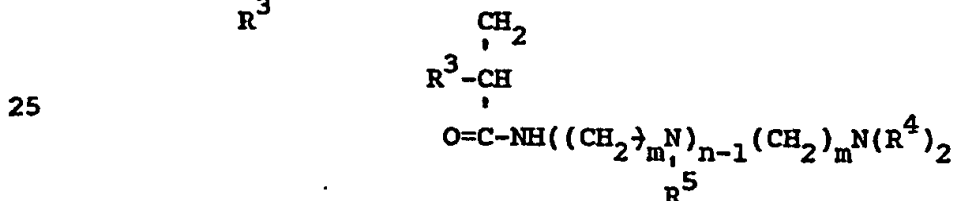
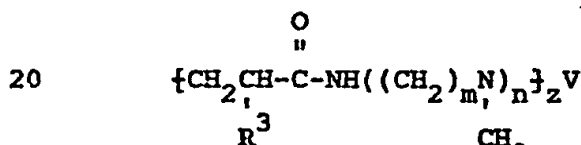
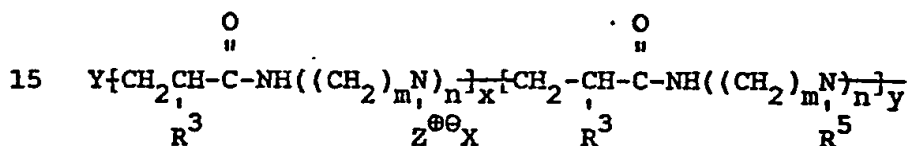
- wherein R<sup>3</sup> and m are as defined hereinbefore and q is  
 25 zero or a whole number from 1 to 2; each R<sup>1</sup> is inde-  
 pendently alkyl, each E is independently oxiranyl or E  
 and R<sup>1</sup> are collectively 2-hydroxypropylene. In the  
 most preferred quaternized polyamidoamines, E and R<sup>1</sup>  
 are collectively 2-hydroxypropylene such that the  
 30 pendant quaternary ammonium moiety contains an azeti-  
 dinium ring and is represented by the formula:



-16-

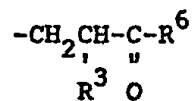


wherein  $\text{R}^3$  is hydrogen or methyl;  $m$  is 2;  $q$  is 0, 1, 2 or 3;  $\text{X}$  is chloride and  $\text{R}^2$  is alkyl, especially methyl, halohydroxyalkyl, especially 3-chloro-2-hydroxy propyl, or epoxy, especially 2,3-epoxy propyl. Preferably, the ammonium polyamidoamines of this invention are random polymers represented by the statistical formula:



wherein  $\text{R}^3$ ,  $\text{Z}^{\oplus}$ ,  $\text{X}^-$ ,  $m$  and  $n$  are as defined hereinbefore;  $\text{Y}$  is a terminal group characteristic of polyamidoamines;  $\text{V}$  is hydrogen or the residue of polymerization to form a polyamidoamine; each  $\text{R}^4$  is independently hydrogen or lower alkyl, e.g.,  $\text{C}_1$ - $\text{C}_3$  alkyl; each  $\text{R}^5$  is independently hydrogen or

-17-

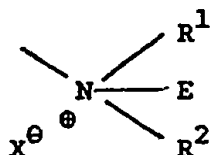


wherein  $\text{R}^3$  is as defined before and  $\text{R}^6$  is  $-\text{NH}_2$ ;  $-\text{OH}$  or  
 5  $-\text{OR}^7$  wherein  $\text{R}^7$  is hydrocarbyl such as alkyl;  $x$  is a  
 whole number from 1 to 1000;  $y$  is 0 or a whole number  
 from 1 to 200; and  $z$  is 0 or a whole number from 1 to  
 200, provided that the ratio of  $x$  to  $(y + z)$  is at  
 least 3:1, most preferably at least 10:1.

10 In the preparation of the ammonium poly-  
 amidoamines of this invention, it is preferred to  
 successively react a linear polyamidoamine with an  
 ethylenically unsaturated carboxylic acid, ester or  
 amide and then with polyamine to form a branched poly-  
 15 amidoamine. The branched polyamidoamine is then con-  
 tacted with epihalohydrin or other compound containing  
 a moiety as defined by E hereinbefore to yield the  
 desired ammonium polyamidoamine wherein the pendant  
 ammonium moiety contains cross-linking functionality.

20 In the conversion of all or a portion of the  
 pendant amine moieties of the branched polyamidoamine  
 to ammonium form, the branched polyamidoamine is con-  
 tacted with an alkylating agent, a mixture of alkylating  
 agents or other agents capable of converting the amine  
 25 to ammonium form such that the pendant amino nitrogens  
 of the branched polyamidoamine are converted to ammonium  
 moieties represented by the following formula:-

-18-



- 5 wherein each  $\text{R}^1$ ,  $\text{R}^2$ , E and  $\text{X}^{\oplus}$  are as defined hereinbefore.

In the preparation of the more preferred quaternized polyamidoamine, the branched polyamidoamine is reacted with an epoxy compound such as an epihalohydrin or an azetidinium forming compound such as a 1,3-dihalo-  
 10 alkane under conditions sufficient to cause the pendant amine groups of the branched polyamidoamine to be alkylated. It is preferred to carry out this alkylation reaction in a solvent. If a solvent system is used in  
 15 the formation of the branched polyamidoamine, then the same solvent or water diluted solvent may be used in the alkylation reaction. Thus, water, lower alkanols such as methanol and mixtures thereof are preferred solvents for the alkylation reaction. In general, sufficient  
 20 solvent is employed to just solubilize the reactants and to permit easy stirring. Generally, solutions containing from 30 to 75 weight percent of the branched polyamidoamine are employed. Following dissolution of the branched polyamidoamine, the epihalohydrin or other  
 25 suitable alkylating agent is added. In the case of epihalohydrin, the reaction is preferably carried out at temperatures in the range from 0 up to about 35°C. The resulting alkylated polyamidoamine, which is prepared using epihalohydrin, contains an epoxy group and/or  
 30 halohydrin groups in the quaternary ammonium moiety. This material may be employed as is as a wet strength

agent or may be converted to an azetidinium ring by dilution with water and heating. Pendant residual halohydrin groups may be converted to epoxy groups by contacting this material with a neutralizing agent for  
5 acid such as sodium hydroxide, calcium carbonate, sodium carbonate, sodium bicarbonate and the like under conditions described by Weissberger in "Heterocyclic Compounds with Three and Four Membered Rings," Inter-  
science Publishers, Part 2, page 891 (1964). In instances  
10 wherein it is desirable to prepare a quaternary ammonium compound in which the amino nitrogen is substituted with an alkyl or hydroxyalkyl group in addition to an epoxy group or an azetidinium ring, the branched polyamidoamine may be first alkylated with an alkyl halide  
15 or hydroxyalkyl halide or alkylene oxide and then subsequently alkylated with epihalohydrin.

The resulting ammonium polyamidoamine is now ready for use as an additive in the manufacture of paper or in the manufacture of textiles.

20 In the manufacture of paper having improved wet and dry strength, the method of the present invention is practiced in the following manner: (1) an aqueous suspension of cellulosic fibers is formed, (2) the ammonium polyamidoamine, advantageously in the  
25 form of a dilute aqueous solution, is added to the suspension and thereby absorbed onto the cellulosic fibers, and (3) the fibers are sheeted and dried using conventional procedures to form the desired cellulosic web.

30 The aqueous suspension of cellulosic fibers is formed in any conventional manner. Usually the

-20-

fibers are beaten and refined, and the suspension is adjusted to convenient consistency, advantageously from 0.1 to 6 weight percent fibers based on the weight of the suspension. Because of the strengthening characteristics of the ammonium polyamidoamine, the amount of beating which is conventionally required can be reduced significantly. In addition, cheaper grades of pulp can be employed in the practice of this invention. The amount of ammonium polyamidoamine added is that which is effective to improve the wet strength of the resulting web of the cellulosic fibers. Such amounts are preferably within the range from 0.1 to 2, especially from 0.25 to 0.75, weight percent based on the dry weight of the cellulosic fiber.

While the particular mode of adding the ammonium polyamidoamine to the suspension of cellulosic fibers is not particularly critical, it is desirable that the particular mode be sufficient to achieve uniform dispersal of the polyamidoamine throughout the suspension in order to ensure uniform absorption of the polymer by the fibers. The addition is therefore most effectively practiced by adding an aqueous solution containing from 0.1 to 10, preferably about 1, weight percent of the polyamidoamine to a turbulent stream of the fibrous suspension at the stock chest or at some other point near the web forming wire. It is suitable, however, to incorporate the polymer in the beater, hydropulper or stock chest. In the latter case, the stock is most advantageously agitated during the addition, and the solution of the polymer is in a rather dilute form. The pH of the cellulosic fibrous suspension may be at any value between 4 and 8, preferably from 6 to 6.

-21-

In addition to the ammonium polyamidoamine, conventional amounts of other additives normally employed in the manufacture of paper such as pigments, fillers, stabilizers, retention aids and the like may be employed.

5 Also, it is found that the addition of various anionic polymers such as polyacrylic acid or partially hydrolyzed polyacrylamides further enhance the strengthening characteristics of the ammonium polyamidoamine. When such anionic polymers are advantageously employed, it

10 is preferred to employ a partially hydrolyzed polyacrylamide having a weight average molecular weight (Mw) from 200,000 to 500,000 and from 5 to 30 mole percent of amide groups converted to acid groups. When used, such anionic polymers are employed in amounts in

15 the range from 0.1 to 1, preferably from 0.4 to 0.7 milliequivalents of anionic moiety of the anionic polymer per milliequivalents of cationic moiety of the ammonium polyamidoamine.

Cellulosic fibers most advantageously treated

20 with the ammonium polyamidoamines of the present invention include bleached and unbleached sulfate (K: ft) pulps, bleached and unbleached sulfite pulps, bleached and unbleached soda pulps, neutral sulfite pulps, semi-chemical and chemical ground wood pulps, ground

25 wood pulps and any combination of such fibers. The foregoing designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are known in the pulp and paper industries.

In addition to the foregoing applications,

30 the ammonium polyamidoamines of the present invention are also usefully employed as antistatic agents and dimension stabilizers for textiles. Textiles beneficially treated with such ammonium polyamidoamines

-22-

include synthetic fibers such as nylon, polyolefins, polyesters and the like as well as blends of such fibers with natural fibers such as cotton, wool and the like.

5 Example 6

A. Quaternization of Branched Polyamidoamine

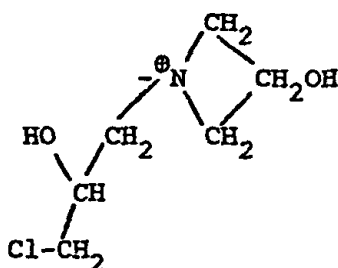
Into a 100 ml, three-neck round bottom flask equipped with an air driven stirrer and thermometer is charged 16.79 g of a 57 percent solution of the afore-  
10 mentioned branched polyamidoamine. The flask is cooled to 5°C and 7.73 g of epichlorohydrin (epi) (1:1 mole ratio of pendant amine hydrogen to epi) is added with stirring to the flask. The reaction mixture is allowed to warm to room temperature over a 7½-hour period and  
15 41.81 g of water heated to 70°C is added. The resulting stirred mixture is heated at 65°C for one hour to yield a clear solution and then allowed to cool to room temperature. A quaternized 100 percent branched polyamidoamine (Wet Strength Additive A) is recovered.

20 For the purposes of comparison, the foregoing quaternization reaction is repeated using 5.42 g of epichlorohydrin and 10.28 g of a 65 percent aqueous solution of a 50 percent branched polyamidoamine. The 50 percent branched polyamidoamine is produced according  
25 to the procedure described hereinbefore except that only 12.27 g (0.5 mole of methyl acrylate per 1 mole of amino hydrogens) is employed. The resulting quaternized 50 percent branched polyamidoamine is Wet Strength Additive B in Table I.

30 Also for comparison, the above quaternization reaction is repeated using 24.2 g of an aqueous solution containing 57 percent of a linear (non-branched)

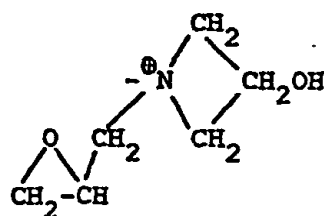
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polyamidoamine produced by the foregoing procedure and 11.19 g of epichlorohydrin to produce a quaternized linear polyamidoamine (Wet Strength Additive C). Also for purposes of comparison, 10.61 g of a 65 percent solid solution of a 100 percent branched polyamidoamine made by the foregoing procedure and 5.60 g of epichlorohydrin (1:1 mole ratio of amine hydrogens to epichlorohydrin) to yield a polymer (Wet Strength Additive D) containing quaternary moieties represented by the following formula:



15

To 22.18 g of a 20 percent solution of this polymer in water is added 0.59 g of an aqueous solution of 50 percent sodium hydroxide and then maintained at room temperature for 6 days. Analysis of the resulting product indicates formation of a (Wet Strength Additive E) polymer having quaternary moieties represented by the following formula:



25



### B. Treated Handsheet Preparation

A 1 percent slurry of bleached hard wood/soft wood Kraft (50/50) pulp is prepared in deionized water, and the pH of the resulting slurry is adjusted to 7.

- 5 An aqueous solution containing 1 percent of a quaternized polyamidoamine as described hereinbefore is added to a 1 liter sample of the pulp slurry (5 cc of the 1 percent solution of polymer equal 10 pounds/ton of pulp). The slurry sample is mixed for 1 minute and
- 10 then added to 7.5 liters of deionized water. The resulting pulp slurry is mixed in the proportionater section of a Noble and Wood apparatus. A 2 liter sample is then taken from the proportionater and added to 10 liters of deionized water in the headbox section.
- 15 Three handsheets (2.5 g) are made from the slurry sample using a Noble and Wood handsheet mold (20 cm x 20 cm). The handsheets are dried on a Noble and Wood drier at 98°C (208°F) to give an average of 4 to 4.5 percent moisture content in the sheets. One-half of
- 20 the sheets are cured at 85°C for 30 minutes in an oven. All of the sheets are soaked for at least one-half hour in deionized water, blotted dry and tested on a Mullins Burst tester. The results are reported as burst values in Table I. For the purpose of comparison, a control
- 25 slurry is prepared which contains no polymeric additive formed into handsheets and tested for wet strength by the foregoing procedure. The results of this test are also recorded in Table I.

TABLE I

Sample No.	Type	Polymeric Wet Strength Additive (1)		Wet Burst, (2)	
		Degree of Branching, mole %	Amount, lb/ton (kg/metric ton)	lb/in <sup>2</sup> (kg/cm <sup>2</sup> ) Uncured	Cured
C*	None	--		2.5	2.7
1	A	100	15	13.5	10.0
2	B	50	15	5.8	2.9
A*	C	0	15	4.0	3.0
3	D	100	10	11.3	7.7
4	E	100	10	14.9	11.8

\* N t an example of the invention.

(1) A - E as defined before in this Example.

Amount in pounds of the named polymeric wet strength additive per ton of pulp.

(2) Test procedure of TAPPI T-403 ts-65 and values calculated according to TAPPI T-220 m-60.

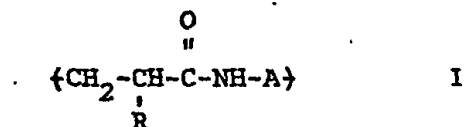
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As evidenced by the data of Table I, ammonium derivatives of branched polyamidoamines are better wet strength additives than ammonium derivatives of linear polyamidoamines.

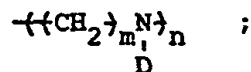
- 27 -

CLAIMS :

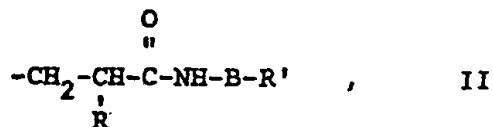
1. A branched polyamidoamine having a weight average molecular weight of at least 550 and consisting essentially of repeating units corresponding to the formula I



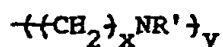
wherein R at each occurrence is independently -H or lower alkyl; A is



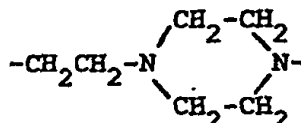
m is an integer of from 2 to 6 and n is an integer of from 1 to 3; D at each occurrence is independently -H or corresponds to the formula II



with the proviso that at least about 10 percent of the groups represented by D correspond to formula II; B is



or



wherein x is an integer of from 2 to 10 and y is an integer of from 1 to 6; R' at each occurrence is independently -H, a C<sub>1</sub> to C<sub>4</sub> alkyl, or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl.

2. A polyamidoamine as claimed in Claim 1 wherein B is  $(\text{CH}_2)_x\text{NR}'\text{--}_y$  and x and m are each independently 2 or 3.

3. A polyamidoamine as claimed in Claim 1 or Claim 2 wherein y and n are each independently 1 or 2.

4. A polyamidoamine as claimed in any one of the preceding claims wherein R' at each occurrence is independently -H, -CH<sub>3</sub> or -CH<sub>2</sub>OH.

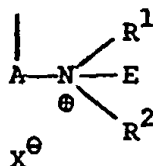
5. A polyamidoamine as claimed in Claim 4 wherein x and m are each 2, y and n are each 1, R' is -CH<sub>3</sub> at each occurrence and R is H at each occurrence.

6. A polyamidoamine as claimed in Claim 4 wherein x and m are each 2, y and n are each 1 and R' and R are H at each occurrence.

- 29 -

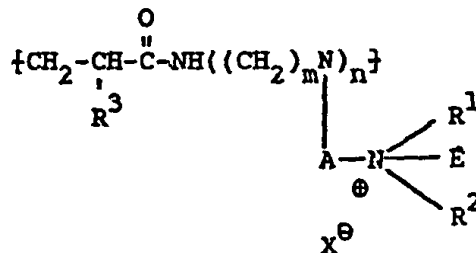
7. A polyamidoamine as claimed in any one of the preceding claims which bears a pendant ammonium moiety having a cross-linking functionality.

8. A polyamidoamine as claimed in Claim 7 wherein the pendant ammonium moiety is represented by the formula:



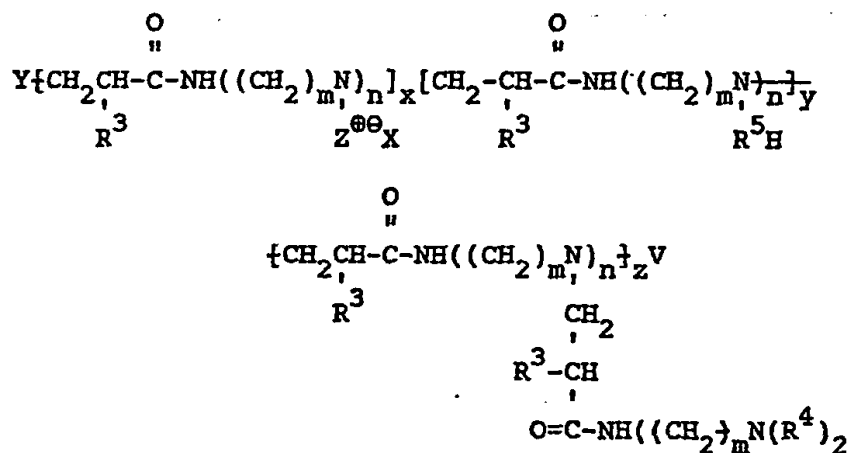
wherein each  $\text{R}^1$  and each  $\text{R}^2$  are independently hydrogen, halohydroxyhydrocarbyl, hydrocarbyl, hydroxyhydrocarbyl or aminohydrocarbyl, wherein amino is a secondary or tertiary amino; E is a monovalent hydrocarbon radical bearing an epoxy group or a group or groups capable of being converted to an epoxy group or E and  $\text{R}^1$  are collectively a propylene radical or substituted propylene radical wherein the  $\alpha$ -carbon substituents are  $\text{C}_1$ - $\text{C}_3$  alkyl and the  $\beta$ -carbon substituent is hydroxy, halo, hydrocarbyl or hydroxyhydrocarbyl; A is a divalent organic radical; X is a monovalent or polyvalent anion common to conventional ammonium salts.

9. A polyamidoamine as claimed in Claim 8 which contains a quaternary ammonium repeating unit represented by the formula:

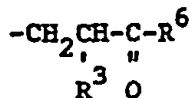


wherein A and X are defined in Claim 8, each  $R^1$  and each  $R^2$  are independently hydrocarbyl, hydroxyhydrocarbyl or aminohydrocarbyl wherein the amino is a secondary or tertiary amino; E is a monovalent hydrocarbon radical bearing an epoxy group or a group or groups capable of being converted to an epoxy group or E and  $R^1$  are collectively a propylene radical or substituted propylene radical wherein the  $\alpha$ -carbon substituents are  $C_1$ - $C_3$  alkyl and the  $\beta$ -carbon substituent is hydroxy, halo, hydrocarbyl or hydroxyhydrocarbyl; A is a divalent organic radical, X is a monovalent or polyvalent anion common to conventional ammonium salts; each  $R^3$  is independently hydrogen or lower alkyl, e.g., methyl or ethyl, each m is a whole number from 2 to 6; and n is a whole number from 1 to 3.

10. A polyamidoamine as claimed in Claim 8, which is a random polymer represented by the statistical formula:

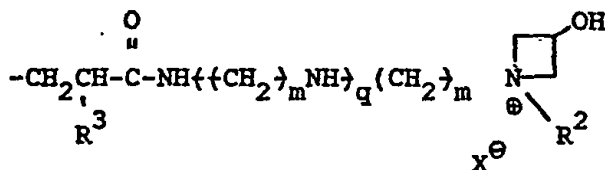


wherein Z is the ammonium moiety; each  $R^3$  is independently hydrogen or methyl; each  $R^4$  is independently hydrogen or lower alkyl; each  $R^5$  is independently hydrogen or



wherein  $R^6$  is  $\text{NH}_2$ , OH or  $\text{OR}^7$  wherein  $R^7$  is hydrocarbyl; Y is a terminal group characteristic of a polyamidoamine; V is hydrogen or the residue of polymerization to form a polyamidoamine; each m is a whole number from 2 to 6; n is 1 or 2; x is a whole number from 1 to 1000; y is 0 or a whole number from 1 to 200; and z is 0 or a whole number from 1 to 200, provided that the ratio of x to (y + z) is at least 3:1.

11. A polyamidoamine as claimed in any one of claims 8 to 10 wherein the pendant ammonium moiety is represented by the formula:



wherein  $R^3$  is hydrogen or methyl; m is 2; q is 0, 1, 2 or 3; X is chloride and  $R^2$  is alkyl, halohydroxyalkyl or epoxy.

12. A polyaminoamide as claimed in Claim 11 wherein  $R^3$  is hydrogen and  $R^2$  is 3-chloro-2-hydroxypropyl or 2,3-epoxypropyl.

13. A method for preparing a branched polyamidoamine comprising the steps of (1) contacting a linear polyamidoamine with an  $\alpha,\beta$ -ethylenically unsaturated carbocyclic compound under conditions whereby



a substituted polyamidoamine is formed, and (2) contacting the substituted polyamidoamine with a polyamine having at least 2 secondary and/or primary amine moieties under conditions whereby a branched amidoamine bearing a pendant amine moiety is formed.

14. A method for preparing the polyamidoamine as claimed in Claim 9 comprising the steps of (1) contacting a linear polyamidoamine with an  $\alpha, \beta$ -ethylenically unsaturated carboxylic compound under conditions whereby a substituted polyamidoamine is formed, (2) contacting the substituted polyamidoamine with a polyamine having at least 2 secondary and/or primary amine moieties under conditions whereby a branched amidoamine bearing a pendant amine moiety is formed, and (3) contacting the branched polyamidoamine with an epihalohydrin under conditions whereby pendant curable ammonium moieties on the branched polyamidoamine are formed.

15. A method for improving the wet strength of paper, comprising the steps of (1) contacting the paper pulp with an amount of the ammonium polyamidoamine as claimed in any one of Claims 7 to 12 which is effective to increase the wet strength of the paper sheet formed from the pulp, (2) forming the pulp into an article of the desired shape and (3) subjecting the article to conditions whereby the polyamidoamine is cross-linked.